九十一學年度 生命科學院四所 碩士班研究生招生考試

科目 有機化學 科號 0902 共 9 頁第 1 頁 *請在試卷【答案卷】內作答

I. Choose a correct answer from each of the following questions. **(40%, 2% each)**

1) Which of the following amino acids has zero optical rotation under all conditions?
   (A) threonine
   (B) proline
   (C) glycine
   (D) alanine

2) Which of the following compounds is not a carbonyl compound?
   (A) aldehyde
   (B) carboxylic acid
   (C) amide
   (D) alcohol

3) Which of the following factors can not determine the intensity of IR absorption?
   (A) number of bonds of the type being observed
   (B) masses of the atoms involved in the bonds
   (C) concentration of the sample
   (D) the change of dipole-moment in the molecule resulting from the bond vibration of interest

4) What is the unsaturation number of $C_3H_4Cl_4$?
   (A) 0
   (B) 1
   (C) 2
   (D) 3

5) Which one of the following information is not available from an NMR spectrum?
   (A) chemical shift
   (B) integral
   (C) wavelength
   (D) splitting

6) In which of the following solvents would you expect hexane to be least soluble?

(A) diethyl ether

(B) methylene chloride

(C) ethanol

(D) 1-octanol

7) Compare the acidity of the following compounds in aqueous solution:

I. $CF_3(CH_2)_2OH$ II. $CH_3(CH_2)_2OH$ III. $(CH_3)_3COH$

(A) I > II > III

(B) I > III > II

(C) II > I > III

(D) III > II > I

8) Compare the ratio of E2 elimination to S_N2 substitution products observed when the following alkoxide bases react with isobutyl bromide:

I. $(CH_3)_2CHO^-$ II. CH_3O^- III. $(CH_3)_3CO^-$

(A) I > II > III

(B) II > I > III

(C) I > III > II

(D) III > I > II

9) Which of the following sets of compounds are enantiomers?

(A) α-D-glucopyranose and β-D-glucopyranose

(B) α-D-glucopyranose and α-D-mannopyranose

(C) β-D-mannopyranose and β-L-mannopyranose

(D) α-D-ribofuranose and α-D-ribopyranose

10) Which of the following amino acids does <u>not</u> react with ninhydrin to give Ruhemann's purple?

(A) arginine

(B) glycine

(C) proline

(D) serine

11) Compare the acidity of the terminal C-H of alkane, alkene, alkyne (in a decreasing order).

(A) alkane, alkene, alkyne

(B) alkyne, alkene, alkane

(C) alkane, alkyne, alkene

(D) alkyne, alkane, alkene

12) Which one of the following compounds is not a Lewis acid?

(A) $:CH_2$

(B) $(CH_3)_3C^+$

(C) $(CH_3)_3B$

(D) $(CH_3)H_3N^+$

13) A sample aspirin (acetylsalicylic acid) contains 60% carbon, 4.4% hydrogen, and 35.6% oxygen. Its molecular weight is 180. What is the molecular formula for aspirin?

(A) $C_6H_{12}O_6$

(B) $C_8H_4O_5$

(C) $C_9H_8O_4$

(D) $C_{10}H_{12}O_3$

14) Which of the following reactions gives a compound with the most electron spin resonance signals?

(A) X-ray irradiation of methyl iodide

(B) X-ray irradiation of ethyl iodide

(C) γ-irradiation of propane

(D) γ-irradiation of n-butane

15) Which of the following compounds are resolvable from its mirror image?

(A) *cis*-1,2-cyclohexanediol

(B) *cis*-1,3-cyclohexanediol

(C) *trans*-1,2-cyclohexanediol

(D) *trans*-1,4-cyclohexanediol

16) The concentration of a cholesterol dissolved in chloroform is 0.06 g/ml. A portion of this solution in a 5-cm polarimeter tube causes an observed rotation of -1.2°. What is the specific rotation of the cholesterol?

(A) +40°

(B) +4°

(C) -4°

(D) -40°

17) How many chiral centers are there in the anti-microbial drug chloramphenicol?

$O_2N(C_6H_5)CHOHCH(CH_2OH)NHCOCHCl_2$

(A) 2

(B) 3

(C) 4

(D) 5

18) When a D-glucose derivative "G" is treated with 4 moles of periodic acid HIO4, 3 moles of HCOOH, 1 mole of HCHO, and 1 mole of OHC–COOH are produced. What modification does G have?

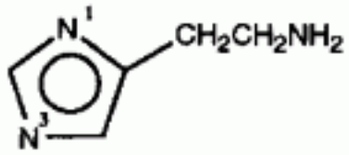
(A) Reduction of C^1 to alcohol

(B) oxidation of C^1 to carboxylic acid

(C) oxidation of C^6 to alcohol

(D) oxidation of C^6 to alcohol

19) Histamine is responsible for many allergenic reaction and has the following structure. What is the relative basicity of the two nitrogens N^1 and N^3?



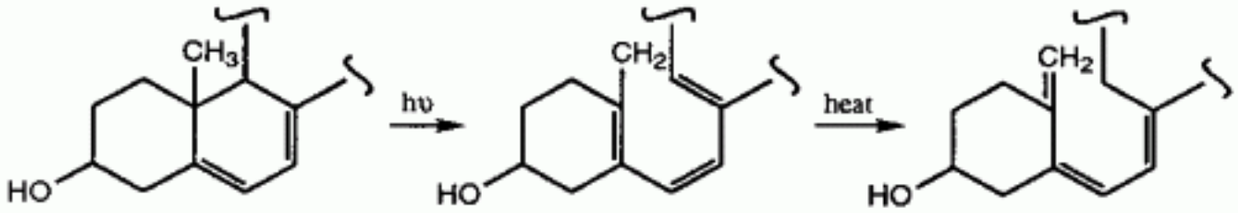
(A) $N^1 > N^3$

(B) $N^1 = N^3$

(C) $N^1 < N^3$

(D) none of them is basic

20. In the skin of animals exposed to sunlight, 7-dehydrocholesterol is converted into hormone cholecalciferol, vitamin D_3, as shown in the following scheme.



7-Dehydrocholesterol Pre-cholecalciferol Cholecalciferol

What chemical processes must take place in the conversion?

I. Thermal ring opening **II.** [1,3] hydride transfer

III. photochemical ring opening **IV.** [1,7] hydride shift

(A) I, II

(B) I, IV

(C) II, III

(D) III, IV

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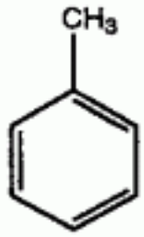
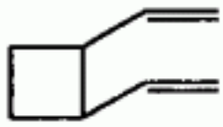
II. Predict the major products **A** to **J** in the following reactions. **(20%, 2% each)**

(1)



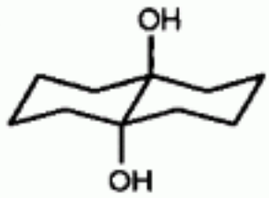
$\xrightarrow{KMnO_4}$ **A** $\xrightarrow[EtOH]{Na/NH_3}$ **B**

(2)



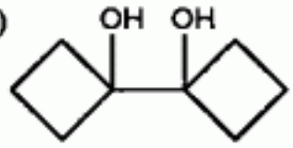
$\xrightarrow[\text{Cope rearrangement}]{\text{heat}}$ **C**

(3)



$\xrightarrow[\text{benzene}]{Pb(OAc)_4}$ **D**

(4)

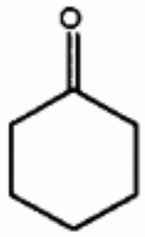


$\xrightarrow{H^+}$ **E**

(5)

$C_6H_5CH{=}CHCHO + Ph_3P{=}CH_2 \longrightarrow$ **F**

(6)



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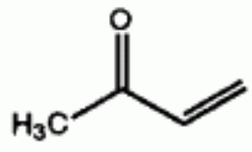
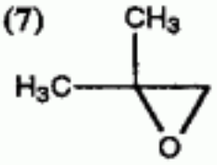


$\xrightarrow{\text{base}}$ **G**

(7)



+ $H_2{}^{18}O \xrightarrow{H^+}$ **H** $\xrightarrow{CH_3ONa}$ **I**

(8)

trans-2-butene $\xrightarrow{Br_2}$ **J**

III. Determine the structures of A, B, C, D, E based on their spectroscopic data. **(20%, 4% each)**

A) $C_6H_{12}O_2$

H^1NMR: δ 1.2 (6H, s); δ 2.15 (3H, s); δ 2.6 (2H, s); δ 3.85 (1H, s)

IR: 1050 cm^{-1}; 1720 cm^{-1}; 3400 cm^{-1} (board)

B) $C_8H_8O_2$

H^1NMR: δ 3.8 (3H, s); δ 7.0 (2H, d); δ 7.8 (2H, d); δ 9.8 (1H, s)

IR: 1050 cm^{-1}; 1688 cm^{-1}; 2750 cm^{-1}; 2820 cm^{-1}

C) $C_5H_8Br_4$

H^1NMR: δ 3.6 (s)

D) $C_9H_{10}O_2$

H^1NMR: δ 2.85 (4H, multiple); δ 7.7 (5H, multiple); δ 10.0 (1H, s)

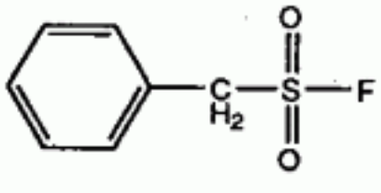
IR: 702 cm^{-1}; 1220 cm^{-1}; 1700 cm^{-1}; 3200-3400 cm^{-1}

E) $C_8H_{11}N$

H^1NMR: δ 1.3 (3H, d); δ 1.35 (2H, s); δ 4.0 (1H, q); δ 7.3 (5H, multiple)

IR: 1600 cm^{-1}; 1640 cm^{-1}; 3200 cm^{-1}; 3400 cm^{-1}

IV. Phenylmethanesulfonyl fluoride (PMSF) is a commonly used protease inhibitor in the laboratory.



(PMSF)

Propose a mechanism by which PMSF inhibits serine protease, like trypsin. (Hint: serine protease has a serine residue in its active site.) **(2%)**

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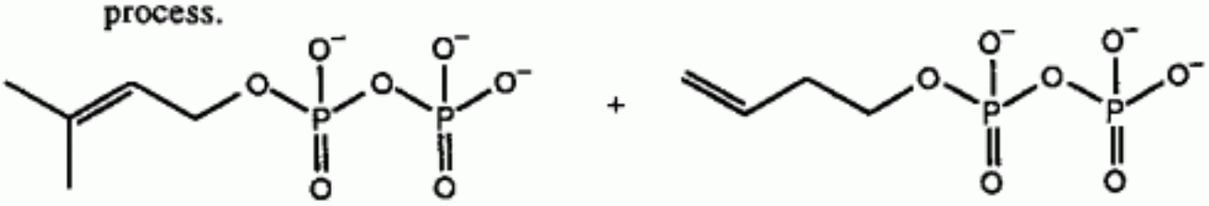
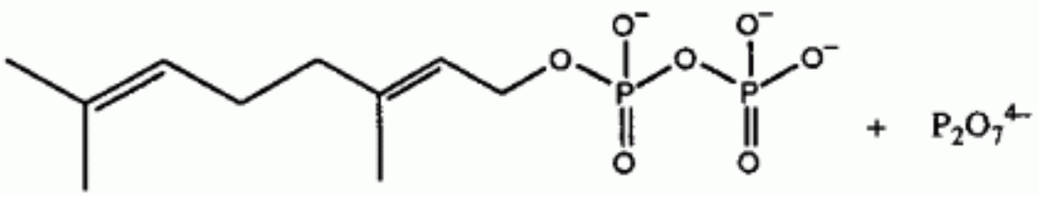
V. An enzyme prenyl transferase catalyzes the following reaction in an S_N1-like process.



γ,γ-dimethylallyl pyrophosphate (DMAP)

isopentenyl pyrophosphate (IPP)

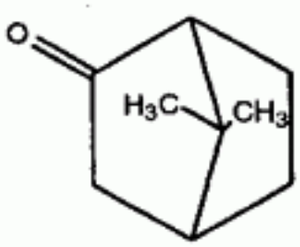
Prenyl transferase



geranyl pyrophosphate (GPP)

Propose the chemical mechanism for this reaction and indicate the intermediate or transition state if any. (5%)

IV. Camphor has two asymmetric carbons, but normally only two optical isomers exist.



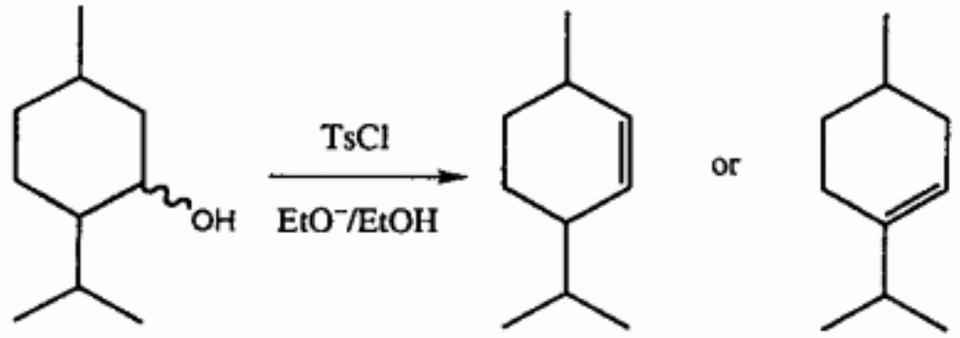
Show the structures of the two isomers and Explain why . (4%)

VII. Eisenine consists of 2 moles of glutamic acid and 1 mole of alanine. However, it has only one free carboxyl group and does not react with the chemical dinitrofluorobenzene. With anhydrous hydrazine, it forms alanine but not glutamic acid.

Determine the structure of eisenine based on its properties (4%)

Detailed analytical steps need to be written or drawn along with your answer.

VIII. Menthol (**I**) is the principal flavoring constituent of peppermint. Its isomer, neomenthol (**II**), differs only in the configuration of the hydroxyl group. In the presence of tosyl chloride and sodium ethoxide in ethanol, **I'** and **II'** are the predominant product of menthol and neomenthol, respectively.



I/II **I'** **II'**

(1) What is the stereochemistry of the hydroxyl in menthol and in neomenthol? Propose a mechanism and explain. **(3%)**

(2) Which of the tosylates (from **I** or **II**) do you predict to react faster? Explain. **(2%)**